PATENT SPECIFICATION (11) 1 521 156

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(21) Application No. 31702/76 (22) Filed 29 July 1976
(31) Convention Application No. 50/092509
(32) Filed 31 July 1975 in
(33) Japan (JP)
(44) Complete Specification published 16 Aug. 1978
(51) INT CL² C08L 29/14 B32B 7/06 (C08L 29/14 83/12)
(52) Index at acceptance
C3M 103 112 126 X
B2E 191 19Y 204 20Y 23Y 285 28Y 297 298 29Y 327 328 348 360 39Y 410 416 417 44Y 477 498 514 568 589
C3T 6D6 6F2 6J4 6J6 6J8

(72) Inventors IWAO MORIYA
TORU SEMA and
SIGEYOSI HATASA

(54) RESIN COMPOSITIONS FOR PEEL-OFF COATINGS

(71) We, THE LION DENTIFRICE CO. LTD., a body corporate organised and existing under the laws of Japan, of 3—7 Honjo 1-chome, Sumida-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to resin compositions for peel-off coatings.

A variety of coating compositions have hitherto been used for forming peel-off coatings or strippable coatings that are serviceable for temporary protection of the surfaces of shaped articles such as, parts of electrical appliances or machines, kitchenwares, and the like. For example, aqueous coating compositions comprising a synthetic resin emulsion, such as, polyvinyl acetate emulsion or an acrylic resin emulsion are most extensively used. Such peel-off coating compositions based on an aqueous polymer emulsion, however, are not satisfactory in storage stability, thermal resistance and water resistance and other properties of the resultant coatings. As a further example are aqueous coating compositions prepared by admixing some floury materials, such as, calcium carbonate, titanium dioxide and the like, silicone resins, and aqueous emulsion of paraffin wax and other supplemental ingredients. These compositions are also defective owing to instability in long storage, delay in drying after application, etc. (See, for example, Japanese Patent Publication No. 14770/73).

Besides, solvent-type compositions for peel-off coating are known. They are prepared by dissolving a polyvinyl butyral resin and a plasticizer in an organic solvent. However, their formulation is disadvantaged by restrictions in the selection and amount of plasticizers to be used. In addition, bleeding or migration of plasticizer often takes place, while the resultant coatings sometimes exhibit low peelability when applied to articles made of certain materials.

According to the invention there is provided a resin composition for peel-off coatings, which comprises

(A) 100 parts by weight of at least one polyvinyl acetal resin, and

(B) 1 to 30 parts by weight of an organopolysiloxane represented by the average formula:

$$\left[(R^1)_m SiO_{\frac{4-m}{2}}\right]_x \left[(R^2)_n SiO_{\frac{3-n}{2}} \left| (CH_2)_a O(C_2H_4O)_b(C_3H_6O)_c H \right.\right]_y \quad (I)$$

where R^1 and R^2 are halogen-substituted or unsubstituted monovalent hydrocarbon groups, m is an integer from 1 to 3, n is 0, 1 or 2, a is 0 or an integer from 1 to 5, b is an integer from 2 to 40, c is 0 or an integer from 1 to 40, and x and y are integers from 2 to 50.

The term "peel-off coatings" as used herein denotes coating films which are formed on the surfaces of a shaped article to temporarily protect the surfaces from outer damages of mechanical or chemical nature during storage and/or transportation and which can be peeled off mainly by hand, without being torn in small pieces

immediately prior to use of the shaped article, so that the intrinsic surfaces of the shaped article are exposed to function.

According to the invention, any solid article, e.g. shaped articles, including parts of electric appliances and machines, kitchen utensils and other kitchen ware, and the like, can be coated with the resin compositions of the invention when temporary protection is required. Further those articles coated with the peel-off coating composition may be used as such and, when the surface of the coating film becomes stained with dirty matter, such as, soot or grease, the coating film may readily be peeled off to expose a fresh surface, which will then be re-coated with the same composition.

Generally it is required that peel-off coatings adhere firmly to the surface of the shaped article without lifting before they are intentionally peeled off. The peelability of the coatings should be maintained through the lapse of time and even in hot conditions. The peel-off coatings should have enough mechanical strengths, water resistance and chemical resistance. On the other hand, the peel-off coating compositions should be suitable for application by any methods, such as, spraying or brushing. The layer of the coating composition applied on various surfaces should promptly dry and form films with a high degree of continuity. The resin compositions of the present invention satisfy all of these requirements.

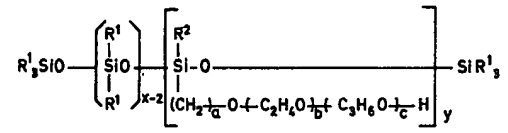
The resin compositions of the invention are applicable to the various surfaces, such as, metals, plastics, ceramics and the like. The coating films formed are clear in appearance and have sufficient hardness, tensile strength and elongation.

The polyvinyl acetal resins as component (A) in the resin compositions for peel-off coatings of the present invention include, for example, polyvinyl formal resins and polyvinyl butyral resins, which are commercially available. It is preferred that the polyvinyl formal resins have a degree of polymerization in the range from 400 to 1,000 and contain at least 30 mole % of the formal component, while the polyvinyl butyral resins have a degree of polymerization in the range from 400 to 1,100 and contain at least 30 mole % of the butyral component. The above-mentioned range of polymerization degree for the polyvinyl formal resins or the polyvinyl butyral resins is not absolutely restrictive, but it may be acceptable that the average of polymerization degrees of any polyvinyl formal resins or polyvinyl butyral resins used falls in the range. Further, component (A) may be a mixture of at least one polyvinyl formal resin and at least one polyvinylbutyral resin.

Next, the organopolysiloxane useful as component (B) in accordance with the present invention is represented by the above-given average formula (I), in which symbols R^1 and R^2 are halogen-substituted or unsubstituted monovalent hydrocarbon groups, such as, alkyl groups (e.g., methyl, ethyl and propyl groups), alkenyl groups (e.g., vinyl, allyl and hexenyl groups), cycloalkyl groups (e.g., cyclohexyl and cycloheptyl groups), aryl groups (e.g., phenyl, tolyl and xylyl groups), aralkyl groups (e.g., benzyl, and phenylethyl groups) and halogen-substituted monovalent hydrocarbon groups (e.g., chlorophenyl, tetrachlorophenyl, chloromethyl and pentafluorobutyl groups).

It is natural that the molecule of component (B) is composed of siloxane units in which the group represented by symbol R^1 or R^2 is not limited to only one specific group. Different R^1 groups and different R^2 groups may be present in the molecule. Similarly, the value denoted by m, n, a, b or c is not limited to one specific value in the molecule.

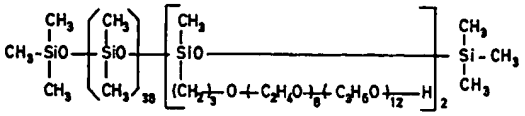
Among the oxyalkylene-containing organopolysiloxanes in conformity with the average formula (I) for component (B) are preferred the linear organopolysiloxanes represented by the following general formula.



(II)

where R^1, R^2, x, y, b and c have the same meanings as defined previously and a' is a positive integer from 1 to 5, from the standpoint of the compatibility of component (B) with component (A) and the stability of component (B) against hydrolysis.

Illustrative of component (B) in the resin composition of the present invention in conformity with the general formula (II) are the organopolysiloxanes expressed by the following formulas.



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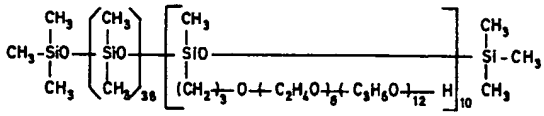

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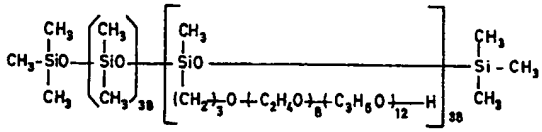

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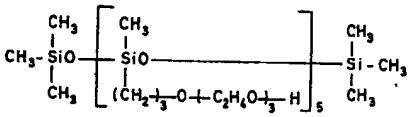

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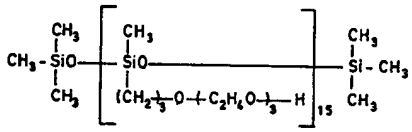

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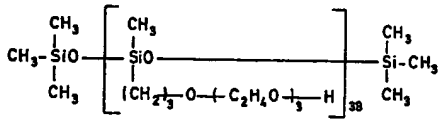

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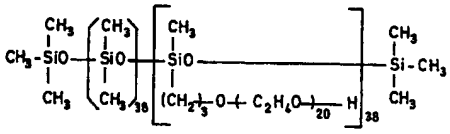

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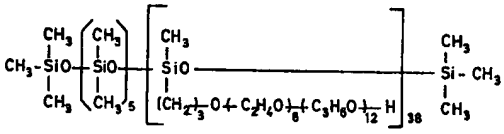
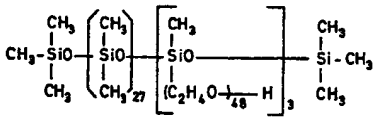


(X)



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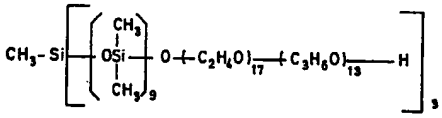
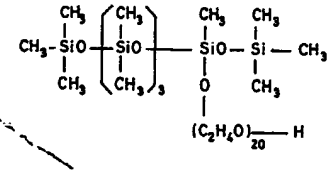


(XII)



(XIII)

The polyoxyalkylene groups in component (B) may be bonded to the silicon atoms through Si—C linkages or Si—O—C linkages, although the Si—O—C linkages are preferred owing to their relatively high stability against hydrolysis. Further these polyoxyalkylene groups have hydroxy groups at the terminals, by which component (B) is rendered sufficiently compatible with component (A), and the coating films formed have excellent physical properties as well as easiness in peeling-off. On the other hand, when the polyoxyalkylene groups bonded to the silicon atoms have a monovalent hydrocarbon group, such as, an alkyl group, an aryl group or the like at the terminals, the organopolysiloxanes concerned have poor compatibility with the polyvinyl acetal resins and cannot be suitable for formulating peel-off coating compositions.

In the resin compositions of the present invention, 1 to 30 parts by weight, preferably 5 to 20 parts by weight of component (B) should be incorporated per 100 parts by weight of component (A). If the amount of component (B) used is smaller than 1 part by weight per 100 parts by weight of (A), the coatings obtained cannot be easily peeled off, while the amount of (B) used in excess of 30 parts by weight brings about inferior properties and economical disadvantages to the resultant coatings.

The resin compositions according to the present invention can be prepared simply by blending component (A) with component (B). In the blending, it is preferred to use an organic solvent or solvents. Included among such organic solvents are alcohols, such as methanol, ethanol, propanol and butanol, aliphatic hydrocarbons, such as hexane and pentane, aromatic hydrocarbons, such as benzene, toluene and xylene, ketones, such as acetone and methyl ethyl ketone, ethers, such as diethyl ether, dioxane and tetrahydrofuran, esters, such as ethyl acetate, propyl acetate and butyl acetate, and chlorinated hydrocarbons, such as trichloroethylene and carbon tetrachloride. When, in particular, the resin composition is to be applied to a shaped article having portions of plastics, for example, from acrylic resin, polystyrene or the like, it is preferred to use alcohols, especially saturated alcohols having 1 to 4 carbon atoms, so that swelling or dissolution of the plastic portion may be prevented. The amount of the organic solvent used is not narrowly critical. In practice the amount of the organic solvent is suitably less than 5% by weight based on the total of components (A) and (B), so as to obtain a suitable viscosity of the coating composition. The organic solvent is added to components (A) and (B) and mixed together with stirring, preferably hot. The temperature, where heat is applied, is suitably in the range 40°—150°C and is suitably chosen depending on the kind, degree of polymerization of the polyvinyl acetal resin. Stirring is suitably continued for from 1 to 6 hours.

In addition to the organic solvents, various other additives, including plasticizers, such as phthalic esters, phosphoric esters, fatty acid esters and glycol derivatives, fatty substances, such as vegetable oils, cellulose derivatives and pigments may be incorporated in the compositions to improve the properties, for example, softness of the resultant coating films.

The resin compositions according to the present invention are useful as the protective coating films for articles, e.g. metal, plastics, and ceramic articles, including articles having painted surfaces. The articles which can be coated include, for example, electric appliances, such as, ventilating fans, kitchen utensils, building materials, and automobiles.

The peel-off coatings can be used not only for the protection of the surfaces of articles during storage or transport prior to use, but also for the protection of the articles during use. When the coated articles become stained on their surfaces during use, the coatings can be readily removed by peeling off and then the exposed surfaces be re-coated with the same composition. Even if the surface to be re-coated is oily or greasy to some extent, the re-coating work can be easily performed to produce new coating films with satisfactory results.

The following examples illustrate the present invention. In the examples, all numerical parts mentioned are parts by weight. In the examples, the peeling-off tests were carried out by the following three methods, involving accelerated aging.

Method I: Clean aluminium plates were coated with the specified peel-off coating compositions, and the resulting coatings were subjected to heat treatment at 80°C for 100 hours, after which their peelability was tested.

Method II: Aluminium plates covered by thin layers of soybean oil were coated with the specified peel-off coating compositions and treated in the same manner as in Method I to test the peelability of the coatings so formed.

Method III: Aluminium, polystyrene resin and glass plates were individually coated with the specified peel-off coating compositions, and the thus resulting coatings were subjected to treatment first by heating at 70°C for 5 hours and then by allowing

to stand at room temperature for 1 hour, such treatment being repeated for 50 cycles. Thereupon, the coatings were tested for peelability.

The results of the peel-off tests are expressed severally by symbols A, B, and C as follows.

A: The coating film was easily peeled off without causing no trouble, for example, tearing in pieces.

B: Part of the coating film was remained unpeeled and adhering to substrate, due to resistance against peeling-off operation.

C: Peeling-off was impossible due to adhesion of the coating film to substrate.

Example 1

Into a vessel equipped with a stirrer were charged 100 parts of a mixed polyvinyl butyral resin composed of *P*(1), *P*(2) and *P*(3) given below in equal amounts, 20 parts of the organopolysiloxane as expressed by the afore-mentioned formula (VIII), 510 parts of methanol and 60 parts of ethanol, followed by mixing with stirring for 2 hours at room temperature, to obtain a clear solution.

P(1): A polyvinyl butyral resin having 2 mole % of unsaponified acetyl groups, 35 mole % of hydroxy groups and 63 mole % of butyral substitution, with a degree of polymerization 1300.

P(2): A polyvinyl butyral resin having the chemical assay identical to *P*(1) but with a degree of polymerization 600.

P(3): A polyvinyl butyral resin having the chemical assay identical to *P*(1) but with a degree of polymerization 400.

The solution of the resin composition thus obtained was applied to an aluminum plate by the brush coating method. The coating film formed was determined with respect to its physical properties and tested for peelability. The results are shown in Table I. In this table and certain tables to follow, "hardness" expressed by mark "H" or "2H" was determined in accordance with the method for determination of hardness by use of pencils as described in Japanese Industrial Standard (JIS) K 5400—1970, 6.14.

TABLE I

Physical Properties:		
	Appearance	Clear
	Hardness	H
	Tensile Strength	200 kg/cm²
	Maximum Elongation	10%
Peelability:		
	In Accordance with Method I	B
	In Accordance with Method II	A

Example 2

The same procedure as in Example 1 was repeated except the stirring of the mixture was carried out at 60°C, instead of room temperature, to obtain a clear solution. Similar tests on the solution resulted as shown in Table II.

TABLE II

Physical Properties:		
	Appearance	Clear
	Hardness	2H
	Tensile Strength	230 kg/cm²
	Maximum Elongation	10%
Peelability:		
	In Accordance with Method I	A
	In Accordance with Method II	A

Example 3

The same procedure as in Example 1 was repeated except that the organopolysiloxane as expressed by the afore-mentioned formula (V) was employed instead of the organopolysiloxane of formula (VIII) to obtain a similarly clear solution. The results of similar tests on the thus obtained solution were as shown in Table III.

TABLE III

Physical Properties:	
Appearance	Clear
Hardness	H
Peelability:	
In Accordance with Method I	B
In Accordance with Method II	A

Example 4

The same procedure as in Example 3 was repeated except that the stirring of the mixture was carried out at 50°C, instead of room temperature, to obtain a clear solution. Similar tests on the solution resulted as shown in Table IV.

TABLE IV

Physical Properties:	
Appearance	Clear
Hardness	2H
Peelability:	
In Accordance with Method I	A
In Accordance with Method II	A

Example 5

Into a vessel equipped with a stirrer were charged 100 parts of polyvinylbutyral resin *P*(2) as used in Example 1, 20 parts of the organopolysiloxane expressed by the afore-mentioned formula (IX), 10 parts of butylphthalylbutyl glycolate, 10 parts of glycerol tributyrate, 240 parts of methanol and 560 parts of ethanol, followed by mixing with stirring at 50°C for 2 hours, to obtain a clear solution.

The thus obtained solution and the coating film formed therefrom were determined with respect to their various properties, and further the coating film was tested for peelability. The results are set out in Table V.

TABLE V

Of the Solution:	
Viscosity at 25°C	200 cps
Surface Tension	15 dynes/cm
Of the Coating Film:	
Tack-free time, at 25°C	5 min.
Tensile Strength	110 kg/cm²
Maximum Elongation	100%
Peelability: In Accordance with Method III;	
Aluminum plate	A
Polystyrene Resin Plate	A
Glass Plate	A

Apart from the above, the same solution of resinous composition was applied on a methylmethacrylate-styrene copolymer resin plate by the aerosol-type spray method. The coating film thus formed was allowed to age at room temperature for 3 months, and then tested for peelability, to find that the peeling operation was easy and the exposed substrate surface was in good conditions.

Example 6

Into a vessel equipped with a stirrer were charged 100 parts of a mixture of polyvinyl butyral resins *P*(1), *P*(2), and *P*(3) in a weight ratio of 2:1:1, 20 parts of the organopolysiloxane as used in Example 5, 10 parts of nitrocellulose, 10 parts of triethyleneglycol and 700 parts of ethanol, followed by mixing with stirring at 60°C for 2 hours, to obtain a clear solution.

The various properties of the thus obtained solution and the coating film formed therefrom as well as the peelability of the coating film were determined in the same fashion as in Example 5, with the results as shown in Table VI.

TABLE VI

Of the Solution:		
	Viscosity, at 25°C	150 cps
	Surface Tension	10 dynes/cm
Of the Coating:		
	Tensile Strength	110 kg/cm²
	Maximum Elongation	100%
Peelability:		
In Accordance with Method III:		
	Aluminium Plate	A
	Polystyrene Resin Plate	A
	Glass Plate	A

Example 7

Into a vessel equipped with a stirrer were charged 100 parts of the same mixed polyvinyl butyral resins as used in Example 1, 20 parts of organopolysiloxane expressed by the afore-mentioned formula (X), 250 parts of methanol and 250 parts of ethanol, followed by mixing with stirring at 60°C for 2 hours, to obtain a clear solution.

The thus obtained solution and the coating film formed therefrom were determined with respect to their various properties and further the coating film was tested for peelability. The results are set out in Table VII.

TABLE VII

Of the Solution:		
	Viscosity, at 25°C	300 cps
	Surface Tension	10 dynes/cm
Of the Coating:		
	Tensile Strength	130 kg/cm²
	Maximum Elongation	100%
Peelability: In Accordance with Method III;		
	Aluminum Plate	A
	Polystyrene Resin Plate	A
	Glass Plate	A

Example 8

Into a vessel equipped with a stirrer were charged 100 parts of a mixture of polyvinyl butyral resins $P(1)$, $P(2)$ and $P(3)$ in a weight ratio of 1:1:1, 20 parts of the organopolysiloxane as expressed by the aforementioned formula (XII), 510 parts of methanol, 60 parts of ethanol, followed by mixing with stirring at 60°C for 2 hours, to obtain a clear solution.

This solution was used to form coating films in the same manner as in Example 1 and the resulting coating films was observed or tested for its various properties and peelability, with the results as shown in Table VIII.

TABLE VIII

Physical Properties:		
	Appearance	Clear
	Hardness	2H
	Tensile Strength	220 kg/cm²
	Maximum Elongation	10%
Peelability:		
	In Accordance with Method I	A
	In Accordance with Method II	A

Example 9

The same procedure as in Example 8 was repeated except only that the organopolysiloxane used was one expressed by the afore-mentioned formula (XIII) instead of formula (XII), to obtain a similarly clear solution. Similar observations or tests were carried out for the coating film formed from the solution, with the results identical to those shown in Table VIII of Example 8.

Example 10

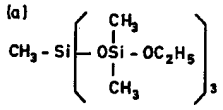
The same procedure as in Example 1 was repeated except that the organopolysiloxane was employed in an amount of 3 parts or 30 parts instead of 20 parts and that the temperature at which stirring was conducted was 60°C instead of room temperature, resulting in producing a similarly clear solution. Similar observations and tests were carried out with the coating films formed from these two solutions, with the results as set out in Table IX.

TABLE IX

Amount of Organopolysiloxane	3 parts	30 parts
Physical Properties:		
Appearance	Clear	Clear
Hardness	2H	2H
Tensile Strength	240 kg/cm²	200 kg/cm²
Maximum Elongation	10%	10%
Peelability:		
In Accordance with Method I	A	A
In Accordance with Method II	A	A

Example 11 (Comparative example only)

(a)



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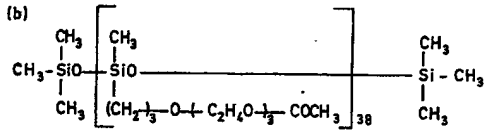

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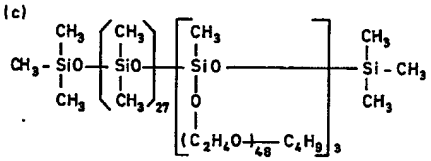
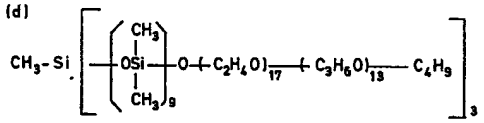
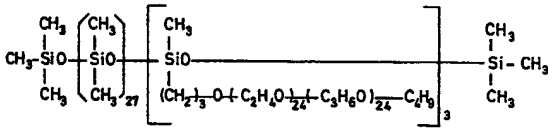


(d)



(e)



Then, using this solution a coating film was prepared in the same fashion as in Example 1 and subjected to observations or tests with respect to its appearance, physical properties and peelability. The results are shown in Table X.

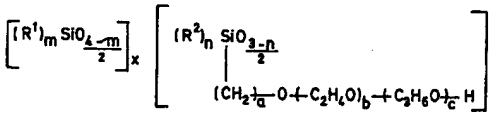
TABLE X

	Organopolysiloxane (a)	(b)	(c)	(d)	(e)
Appearance	Opaque	Translucent	Opaque	Opaque	Opaque
Hardness	2H	2H	2H	2H	2H
Tensile strength, kg/cm²	260	230	*	*	*
Maximum elongation, %	10	10	*	*	*
Peelability:					
Method I	C	C	C	C	C
Method II	B	B	B	B	B

* Film obtained was of dimensions insufficient for determining the property.

WHAT WE CLAIM IS:—

1. A resin composition for peel-off coatings, comprising
(A) 100 parts by weight of at least one polyvinyl acetal resin, and
(B) from 1 to 30 parts by weight of an organopolysiloxane represented by the average formula,



where R^1 and R^2 are halogen-substituted or unsubstituted monovalent hydrocarbon groups, m is an integer from 1 to 3, n is 0, 1 or 2, a is 0 or an integer from 1 to 5, b is an integer from 2 to 40, c is 0 or an integer from 1 to 40, and x and y are integers from 2 to 50.

2. A resin composition as claimed in claim 1, wherein component (A) is a polyvinyl butyral resin.

3. A resin composition as claimed in claim 1, wherein component (A) is a polyvinyl formaldehyde resin.

4. A resin composition as claimed in claim 2, wherein said polyvinyl butyral resin has an average degree of polymerization of between 400 and 1,100, and contains at least 30 mole % of butyral component.

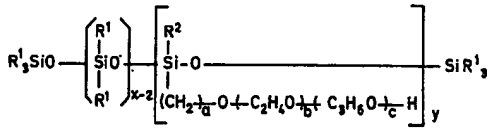
5. A resin composition as claimed in claim 3, wherein said polyvinyl formaldehyde resin has an average degree of polymerization of between 400 and 1,000, and contains at least 30 mole % of formaldehyde component.

6. A resin composition as claimed in any preceding claim, wherein component (B) is present in a proportion of from 5 to 20 parts by weight per 100 parts by weight of component (A).

7. A resin composition as claimed in any preceding claim, wherein each of groups R^1 and R^2 is an alkyl group, alkenyl group, cycloalkyl group, aryl group, aralkyl group or a halogen-substituted monovalent hydrocarbon group.

8. A resin composition as claimed in any preceding claim, which has been obtained by heating a mixture of components (A) and (B) at a temperature in the range from 40 to 150°C for 1 to 6 hours.

9. A resin composition for peel-off coatings,
(A) 100 parts by weight of at least one polyvinyl acetal resin, and
(B) from 1 to 30 parts by weight of an organopolysiloxane represented by the formula



where R^1 and R^2 are halogen-substituted or unsubstituted monovalent hydrocarbon groups, a' is an integer from 1 to 5, b is an integer from 2 to 40, c is 0 or an integer from 1 to 40, and x and y are integers from 2 to 50.

10. A resin composition according to claim 1, wherein component (B) has any one of formulae (III)—(XIII) given hereinabove.

11. A resin composition according to claim 1, substantially as described herein with respect to any one of the compositions described in the foregoing Examples.

12. A solid article having a surface coated with a coating film comprising a resin composition as claimed in any preceding claim.

13. An electrical appliance or kitchen utensil when coated with a coating film as defined in claim 2.

14. A resin solution for coating articles with resin, which comprises a composition as claimed in any one of claims 1—11 in solution in an organic solvent for the resin composition.

15. A resin solution as claimed in claim 14 which has been heated at a temperature of from 40°—150°C, for from 1 to 6 hours.

16. A method of coating an article which comprises brushing or spraying the surface of the article with a solution as claimed in claim 14 or 15 and drying or allowing to dry the solution so applied, to form a surface coating of resin film.

17. A method of preparing a resin composition or solution according to any one of claims 1—11 or 14—15, which comprises blending components (A) and (B) as defined in claim 1.

18. A method according to claim 17, substantially as hereinbefore described with reference to any one of the compositions of the foregoing Examples.

For the Applicants:
D. YOUNG & CO.,
Chartered Patent Agents,
9 & 10 Staple Inn,
London, WC1V 7RD.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.